Legacy Lead Stored in Catchments Is the Dominant Source for Lakes in the UK: Evidence from Atmospherically Derived ^{210}Pb

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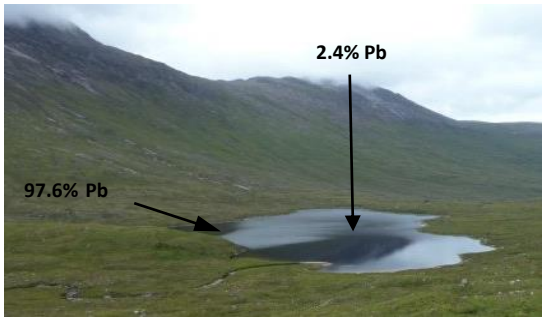
ABSTRACT

There has been a considerable reduction in anthropogenic lead (Pb) emission to the atmosphere in recent decades. However, reduction in Pb inputs to many lakes does not match this as Pb stored in catchment upper soil layers, derived from previous deposition, has become an important source although it is difficult to assess quantitatively. This work uses atmospherically deposited ^{210}Pb as tracer to track Pb movement and so is able, for first time to calculate the relative Pb inputs from direct atmospheric deposition and catchment sources to lakes in the UK directly. Within individual lake sites, ratios of ^{210}Pb/Pb in the catchment terrestrial mosses were normally an order of magnitude higher than those in the catchment surface soils, trapped lake sediments and the surface sediments in the lake-bottom. The results suggest that Pb isotope signatures in the mosses are close to or dominated by atmospheric depositions, and it is reasonable to use ratios of ^{210}Pb/Pb in terrestrial mosses collected from

the lake sites with high annual rainfall over 2000 mm to represent those in atmospheric depositions. It reveals that, after reduction in Pb emission, catchment Pb inputs now typically account for more than 95% of the total Pb entering the lakes.

Abstract Art



1. INTRODUCTION

Although substantial amounts of Pb from anthropogenic sources have entered the atmosphere ever since ancient times, the extent of these emissions increased dramatically following the onset of the industrial revolution in the late 18th century, and reached a peak in the early 1970s when global Pb production exceeded 250,000 tonnes per year [1]. Although much of the Pb emitted into the atmosphere is deposited relatively close to its source, a significant fraction is attached to fine particulates and these may be transported over large distances before being deposited onto the landscape, causing pollution even in relatively remote areas. The bulk of this fallout Pb will be stored in the upper layers of catchment soils [2-4], though a fraction will accumulate in natural archives such as lake sediments or peat bogs [5,6].

Official records from many countries show that since the early 1970s there has been a significant reduction in Pb emissions to the atmosphere. During this period UK emissions have fallen by over 99%, from 9,300 tonnes per year in 1973 to 63 tonnes per year in 2013 [7]. This has resulted in a corresponding decline in Pb fallout [8]. The global nature of this decline has

been confirmed by reconstructions of atmospheric pollution history obtained from records in ombrotrophic peat bogs [9], which receive their nutrients solely from atmospheric deposition. Today, Pb concentrations in the surface layers of peat bogs in northern Alberta, Canada are comparable to the "cleanest" peats formed 6000 to 900 years ago in the Northern Hemisphere[10].

Although Pb concentrations in lake sediments have also shown a decline in many relatively remote lakes,[5,11,12] in the UK lakes, these reductions are small and not comparable with the scale of Pb emission and deposition reductions over the same period. Farmer et al[13] compared adjacent Pb records in lake sediment and peat cores in the remote Cairngorm Mountains in Scotland and found that anthropogenic Pb fluxes had declined to a very low level in the peat cores, but remained elevated despite some reduction in the lake sediment cores. Since Pb stored in catchment soils may be a considerable source to lakes,[6,14] it is likely that re-mobilised catchment Pb has been transferred to the lakes and delayed their "recovery". However, the scale by which this stored Pb in the catchment affects the lake system is not well known, and it is a challenge to environmental geochemists to determine the long-term impact of these catchment sources on Pb pollution in aquatic systems [10]. Understanding and quantifying these processes has an added urgency in view of the likelihood that climate change will bring more frequent, extreme weather events,[15] given rise to accelerated rates of soil erosion, and in consequence, accelerated rates of transport of catchment-stored pollutants into lakes. In this study we used a recently developed ^{210}Pb tracer method[16] to quantitatively determine, for the first time, the scale of Pb derived from catchment inputs to five UK lakes.

The method of using ^{210}Pb to trace Pb sources was introduced in Yang & Appleby.[16] Background and theory for this study are described in the Supporting Information (SI). In this study, we define a parameter η as the ratio of atmospherically delivered ^{210}Pb to Pb.

Atmospherically delivered (fallout) ^{210}Pb fallen to the ground that forms unsupported ^{210}Pb. The fallout Pb and ^{210}Pb concentrations in freshly deposited lake sediment samples will include contributions both from contemporary fallout directly onto the surface of the lake, and historical fallout originally deposited in the catchments [14]. η_d is the ^{210}Pb/Pb ratio in the component attributable to direct (contemporary) fallout, and η_c is the unsupported ^{210}Pb/total Pb ratio in the allochthonous inputs from the catchment. Writing F_d for the fraction of Pb in freshly deposited lake sediments that can be attributed to direct fallout, the ^{210}Pb/Pb ratio in these sediments will be

$$\eta = F_d\eta_d + (1-F_d)\eta_c . \quad (1)$$

The value of η can be determined directly from measurements of ^{210}Pb and Pb on freshly deposited sediments. The value of η_c can be estimated from similar measurements carried out of surficial catchment soils representative of allochthonous inputs to the lake. The direct fallout fraction F_d can be then calculated using the equation

$$F_d = \frac{\eta - \eta_c}{\eta_d - \eta_c} \quad (2)$$

2. METHODS

2.1. Site selection and sample collection. In order to test the methodology, we analysed samples from 5 lakes selected from the UK Upland Waters Monitoring Network: Loch Coire Fionnaraich, Loch Chon, Round Loch of Glenhead, Burnmoor Tarn and Llyn Llagi (Figure 1). They are all upland lakes, to the west of the UK, located in areas of sensitive geology and elevated rainfall.[17] All the sites receive anthropogenic Pb solely from atmospheric deposition.

Figure 1. Map showing the locations of the lake sites where samples were collected.

To determine the ^{210}Pb/Pb ratio in direct fallout (η_d), samples of new moss growth (identified as being less than 1 year) were collected from the terrestrial mosses *Pleurozium schreberi* and *Hylocomium splendens* at each site in open catchment areas. During sample collection, plastic gloves were worn and the sample leaves rinsed with deionized distilled water to remove surface dust before being placed separately in polyethylene bags. They were then stored cold prior to being analyzed. To determine the unsupported ^{210}Pb/Pb ratio in allochthonous catchment inputs (η_c), soil samples were collected from flat representative areas of each catchment as well as likely in-wash routes from around the lake. These were collected using a stainless-steel knife and placed in polyethylene bags. Lead-210/Pb ratios in fresh sediments (η) from each lake were determined using samples collected in sediment traps placed in the water column, and also surficial samples from sediment cores collected from the deepest area of the lake. The sediment traps (triplicate cylinders with a height:diameter ratio larger than

7) were located in deep water areas 1.5 m above the sediment surface to minimize the effect of sediment resuspension [18]. They have been deployed in each UWMN lake since 1991, emptied and re-deployed annually. The cores were collected using gravity cores [19] and extruded vertically in the field at 0.5 cm intervals using a stainless-steel slicer. The uppermost 0–1 cm from each core were placed in individual polyethylene bags and stored cool until analysis. All samples used in this study were collected in July and August 2013 and freeze-dried prior to analysis.

2.2. Total Pb Analysis. 0.2 g moss samples were accurately weighed (4 d.p.) into a 50 mL polypropylene DigiTUBE (SCP Science) and digested on a hotplate for 2 h at 100 °C using 6 mL concentrated HNO3, and then diluted to 50 mL. The digested solutions were analysed using ICP-MS (Bruker aurora M90 ICP-MS). Standard vegetation reference materials were digested and analysed. Standard errors for the analysis were estimated to be less than 10%. Soil and sediment samples were analysed by using a Spectro XLAB2000 X-ray fluorescence (XRF) spectrometer. Standard sediment and soil reference materials were measured. All the standard reference materials had recovery value in the range of 95 -102%. A conservative figure of 10% for standard errors has been used in all calculation.

2.3. Lead-210 Analysis. All the dried samples were analysed for ^{210}Pb and ^{226}Ra by direct gamma assay in the Environmental Radiometric Facility at University College London, using ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detector. Lead-210 was determined via its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV gamma rays emitted by its daughter isotope ^{214}Pb following three weeks storage in sealed containers to allow radioactive equilibration. The absolute efficiencies of the detector were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self-absorption of low energy gamma rays within the sample [20]. In each sample unsupported ^{210}Pb activity, the atmospheric deposited component,

was calculated by subtracting supported ^{210}Pb (i.e. ^{226}Ra) activity from total ^{210}Pb activity. Standard errors (1σ) have been calculated from the counting statistics.

3. RESULTS AND DISCUSSION

3.1. Lead and ^{210}Pb in Mosses. Mosses do not have a developed root system or water-conductive tissue, and the great majority of moss species have been found to obtain most of their nutrient supply from the atmosphere.[21] Since trace metal uptake takes place through the leaf surface of the mosses, terrestrial species such as *Pleurozium schreberi* and *Hylocomium splendens* have been widely used as bio-monitors for trace metal deposition (cf [22, 23]) and provide a means by which to determine time integrated deposition over the period of sampled growth, rather than a snapshot of rainfall event. Therefore, they reflect general state of deposition for the growth period. For this reason, ^{210}Pb/Pb ratios in terrestrial mosses collected in this study could therefore, be used to represent contemporary atmospheric deposition. Unsupported ^{210}Pb and Pb concentrations as well as ^{210}Pb/Pb ratios in the moss samples from each lake catchment are given in Table 1.

145 **Table 1.** Unsupported ^{210}Pb, Pb and ^{210}Pb/Pb ratios (η_d) in moss *Pleurozium schreberi* (PS)
146 and *Hylocomium splendens* (HS) samples collected from the lake catchments.

Sites	Annual rainfall	Species	^{210}Pb		Pb		^{210}Pb/Pb (η_d)	
	mm		Bq kg^{-1}	±1σ	mg kg^{-1}	±1σ	Bq mg^{-1}	±1σ
Loch Coire	3300	PS	490	26.9	0.62	0.06	790	88
Fionnaraich		HS	489	31.6	0.59	0.06	829	100
						Mean value	810	
Loch Chon	2250	PS	295	23.5	1.28	0.13	230	30
		HS	218	19.7	0.88	0.09	248	34
						Mean value	239	
Round Loch of	2300	PS	573	45.7	1.78	0.18	322	41
Glenhead		HS	485	25.8	2.11	0.21	230	26
						Mean value	276	
Burnmoor Tarn	2200	PS	1152	38.4	4.32	0.43	267	28
		HS	913	38	3.97	0.4	230	25
						Mean value	249	
Llyn Llagi	3000	PS	678	31.4	2.59	0.26	262	29
		HS	491	27.7	2.17	0.22	226	26
						Mean value	244	

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148 Annual rainfall for these sites are all high, ranging from 2250 to 3300 mm per year [17].
149 Rainfall is regular in these sites with a high number of rain days and short periods without
150 precipitation, providing ample rain water for moss growth[24]. Although ^{210}Pb activities in the
151 moss samples from Burnmoor Tarn were high compared with the other sites, Pb concentrations
152 were correspondingly high (4 and 4.3 mg kg^{-1}, Table 1) and the ^{210}Pb/Pb ratio comparable to
153 all sites (η_d in a range of 230-280 Bq mg^{-1}) other than Loch Coire Fionnaraich (810 Bq mg^{-1})
154 in north-west Scotland. The low value of this ratio at Loch Coire Fionnaraich is mainly likely
155 driven by the very low Pb concentrations (0.6 mg kg^{-1}) and attributable to low anthropogenic
156 inputs. This loch is the UK UWMN control site due to its remoteness from industrial sources.

157 **3.2. Lead and ^{210}Pb in the catchment soils.** Corresponding results for the catchment
158 soils are given in Table 2. Unsupported ^{210}Pb activities in the surface soils have relatively high
159 values and with most are over 500 Bq kg^{-1} (Table 2). This is due to relatively high ^{210}Pb
160 deposition fluxes and peaty soils in the catchments that have a strong absorption for Pb.

Background Pb concentrations in UK peat soils are normally in a range of 10 to 40 mg kg^{-1} [3,4,25] and surface soils at Loch Coire Fionnaraich and Loch Chon show little evidence for Pb contamination above this background. Loch Chon has been contaminated in the past,[12] but the low Pb concentrations in the surface soils collected from the site are likely due to the massive reductions in Pb emissions since the 1970s. However, in the other three sites, most surface soils still show evidence for Pb pollution (Table 2), some of which is considerable (enrichments of Pb are up to 10, even assuming that the background is 40 mg kg^{-1}).

Although at each site there was quite a lot of variation in the ^{210}Pb/Pb ratio (η_c) between different samples, mean values were relatively consistent. The Welsh, Cumbrian and Galloway sites all had very similar mean values of around 7–8 Bq mg^{-1}. Higher values at Loch Chon (11 Bq mg^{-1}) and Loch Coire Fionnaraich (38 Bq mg^{-1}) were mainly driven by lower Pb concentrations. Lead-210/Pb ratios overall were an order of magnitude lower than in the moss samples. After being deposited to the soil surface ^{210}Pb decays with time, but Pb concentrations remain largely unchanged and so the ^{210}Pb/Pb ratio becomes reduced. The three highest ^{210}Pb/Pb ratios (30 – 70 Bq mg^{-1}, Table 2) are for surface peaty soils collected from Loch Coire Fionnaraich and Round Loch of Glenhead, both of which contained considerable recent moss remains.

178 **Table 2.** Unsupported ^{210}Pb, Pb and ^{210}Pb/Pb ratios (η_c) in catchment soils of the lakes.

Sites	Soil samples	^{210}Pb		Pb		^{210}Pb/Pb (η_c)	
		Bq kg^{-1}	±1σ	mg kg^{-1}	±1σ	Bq mg^{-1}	±1σ
Loch Coire Fionnaraich	soil 1, 0-1cm	1059	80	35	3.5	30	3.8
	soil 2, 0-1 cm	1090	70	15.5	1.5	70	8.2
	stream 1, 0-1 cm	636	43	42.4	4.2	15	1.8
					Mean value	39	
Loch Chon	soil 1, 0-1 cm	670	50	39.8	4	16.8	2.1
	soil 2, 0-1 cm	460	46	37.3	3.7	12.3	1.7
	soil 3, 0-1 cm	214	27	44.3	4.4	4.8	0.77
					Mean value	11	
Round Loch of Glenhead	stream 1-1, 0-1 cm (plant debris rich)	248	11	76.6	7.6	3.2	0.35
	stream 1-2, 0-1 cm (clay rich)	135	8.9	57.1	5.7	2.4	0.28
	stream 2-1, 0-1 cm (coarse sand rich)	96	5.1	28.4	2.8	3.4	0.38
	stream 2-2, 0-1 cm (organic rich)	578	12	153.9	15.4	3.8	0.38
	soil 1, 0-2cm	1138	26	224.8	22.5	5.1	0.52
	soil 1, 2-5cm	552	34	416.9	41.7	1.3	0.16
	soil 2, 0-1cm	446	17	143.1	14.3	3.1	0.33
	soil 2, 1-3cm	578	31	396.8	39.7	1.5	0.16
	soil 3, 0-2cm	899	40	21.2	2.1	42.4	4.6
	soil 3, 2-7cm	424	20	243.1	24.3	1.7	0.19
					Mean value*	3	
Burnmoor Tarn	soil 1, 0-1 cm	784	32	90.6	9.1	8.6	0.9
	soil 2, 0-1 cm	702	63	87.2	8.7	8.0	1.1
	soil 3, 0-1 cm	1275	62	155	15.5	8.2	0.9
	stream 1-1, 0-1 cm (plant debris rich)	642	47	93.9	9.4	6.8	0.8
	stream 1-2, 0-1 cm (organic rich)	687	45	176	17.6	3.9	0.5
	stream 2, 0-1 cm (organic rich)	1408	25	218	21.8	6.5	0.7
					Mean value	7	
Llyn Llagi	soil 1, 0-1 cm	720	36	60.8	6.1	11.8	1.3
	soil 2, 0-1 cm	1446	58	365	36	3.9	0.42
	stream 1, 0-1 cm (organic rich)	1205	57	129.4	12.9	9.3	1.02
	soil 4, 0-1 cm	727	55	202	20.2	3.6	0.45
	soil 5, 0-1 cm	373	17	25	2.5	14.8	1.6
	soil 6, 0-1 cm	346	21	89.3	8.9	3.9	0.45
					Mean value	8	

179 * The mean value for Round Loch of Glenhead excludes the anomalous 0-2cm soil 3 sample.

180

In Round Loch of Glenhead, the catchment geology is mainly tonalite with granite, and Pb concentrations in these are normally around 14.2 mg kg^{-1},[26] and 20 mg kg^{-1},[27] respectively. A coarse sand-rich sample taken from the surface of a stream bed (stream 2 , Table 2) at Round Loch of Glenhead had a Pb concentration of 96 mg kg^{-1}, while an adjacent organic-rich sample in the same stream had a Pb concentration of 578 mg kg^{-1}. However, the ^{210}Pb/Pb ratios in these two samples are very similar (Table 2), and the slightly lower value in the coarse-sand rich sample may be caused by the Pb in the sands, as pollution Pb and atmospherically deposited ^{210}Pb are likely mainly adsorbed to the surfaces of the coarse sands. This indicates that while the concentration and activity of Pb and ^{210}Pb may be altered, if they are from the same source, the ratio of ^{210}Pb/Pb will remain the same.

In each site, these soil samples were collected around the lake where the soils are most likely to be washed into the lake or most representative areas of the catchment. Hence, these soils have potential in affecting catchment Pb and ^{210}Pb inputs to the lake.

3.3. Lead and ^{210}Pb in Trapped and Surface Sediments. When fallout Pb and ^{210}Pb enter the lake water either from the catchment or through direct atmospheric inputs, most of them are transported rapidly by particulate matter and deposited to the lake bottom[28]. Settling particulate matter collected in sediment traps represents an integrated combination of both catchment inputs and direct atmospheric inputs [29]. Properly designed sediment traps collect time-integrated samples of these inputs with an efficiency of 90% or more [30, 31]. Samples of this material were collected from the water column using suitably placed sediment traps as described in the method section, and from the bed of the lake using sediment corers. Results of the ^{210}Pb and Pb measurements on these samples are shown in Table 3.

Unsupported ^{210}Pb activities in the trapped sediments were relatively high, ranging from 770 Bq kg^{-1} in Loch Coire Fionnaraich to 3089 Bq kg^{-1} in Burnmoor Tarn (Table 3).

205 Excluding Burnmoor Tarn, activities in the surficial sediments were consistently around 25%
206 lower. Noting that the uppermost 1 cm can span a period of up to 10 years, two possible factors
207 contributing to this discrepancy are radioactive decay, and partial mixing of the surficial
208 sediments. The very much larger discrepancy in Burnmoor Tarn is almost certainly due to loss
209 of modern sediments from the top of the core. Two earlier cores collected in 1979 and 1989
210 both had much higher surficial concentrations of around 1500 Bq kg^{-1}. Pb concentrations were
211 lowest in Loch Coire Fionnaraich (mean value 37 mg kg^{-1}) and highest in Round Loch of
212 Glenhead (mean value 234 mg kg^{-1}). These two sites also had the lowest and highest ^{210}Pb/Pb
213 ratios, mean values of which ranged from 5 Bq mg^{-1} in Glenhead to 18 Bq mg^{-1} in Fionnaraich.
214 The value for Burnmoor Tarn (17 Bq mg^{-1}) has been calculated from the trap samples alone. A
215 much smaller discrepancy between Pb concentrations in the trap and core samples may indicate
216 relatively constant inputs of Pb in recent years.

217

Table 3. Unsupported ^{210}Pb, Pb and ^{210}Pb/Pb ratios (η) in trapped sediments and surface sediments of the core taken from the lakes.

Sites	Components	^{210}Pb		Pb		^{210}Pb/Pb (η)	
		Bq kg^{-1}	±1σ	mg kg^{-1}	±1σ	Bq mg^{-1}	±1σ
Loch Coire	Trapped	770	54.9	39.5	3.9	19.5	2.4
Fionnaraich	0-0.5 cm	643	37	35.1	3.5	18.3	2.1
	0.5-1 cm	489	32.9	35.1	3.5	13.9	1.6
					Mean value	18	
Loch Chon	Trapped	1305	50.8	132.1	13.2	9.9	1.1
	0-0.5 cm	627	70	93.2	9.3	6.7	1.0
	0.5-1 cm	1101	38.9	145.8	14.6	7.6	0.8
					Mean value	9	
Round Loch	Trapped	1430	78.3	226.9	22.7	6.3	0.7
of Glenhead	0-0.5 cm	1165	18.4	246.6	24.7	4.7	0.5
	0.5-1 cm	920	50.3	234.5	23.4	3.9	0.4
					Mean value	5	
Burnmoor	Trapped	3089	78	187.3	18.7	16.5	1.7
Tarn	0-0.5 cm	120	8.8	62.3	6.2	1.9	0.2
	0.5-1 cm	240	10.6	75.1	7.5	3.2	0.3
					Mean value*	17	
Llyn Llagi	Trapped	1906	60.8	156.7	15.7	12.2	1.3
	0-0.5 cm	1525	61.8	158.4	15.8	9.6	1.0
	0.5-1 cm	1357	53.9	183.5	18.4	7.4	0.8
					Mean value	10	

* Includes only the value from trapped sediments

Unsupported ^{210}Pb activity and Pb concentration in trapped sediments are higher than those in the mosses collected from the catchment of the same lake for all sites, suggesting enrichment of ^{210}Pb in the trapped sediments, and possible catchment input of Pb to the lake. Mean ^{210}Pb/Pb ratios for each site based on both the trapped sediments and surface sediments (5 – 18 Bq mg^{-1}, η) are again an order of magnitude lower than in the corresponding moss samples (240 – 810 Bq mg^{-1}, η_d), slightly lower than in the catchment soils at three sites and slightly higher at the other two.

3.4. Lead Contribution to the Lakes. Although the general comparability between ^{210}Pb/Pb ratios in fresh sediments and catchment samples suggests that inputs of Pb to the lake

via direct fallout are no more than a few percent of total inputs, the fact that at three sites mean catchment ratios are slightly higher than in fresh lake sediments shows that the catchment samples are not truly representative of allochthonous inputs to the lake. One possible cause of the discrepancy is the disproportionate influence of obvious outriders such as the 0-2 cm soil sample 3 from Round Loch of Glenhead (Table 2). Excluding that sample the mean ^{210}Pb/Pb ratio in the Round Loch of Glenhead catchment samples falls from a value significantly above that for fresh sediments to a value significantly below. A second possible cause is under-representation of the minerogenic Pb content in catchment inputs. For example, the 0-1 cm soil samples 1 and 2 from Loch Coire Fionnaraich and the 0-2 cm soil sample 3 from Round Loch of Glenhead (^{210}Pb/Pb ratios in 30 – 70 Bq mg^{-1}, see Table 2) were collected from relatively flat, open peaty areas, which account for considerable parts of the lake catchments. The peaty samples contain high fraction of recently dead mosses, and the soils in these flat, open areas are relatively stable, and are less likely to be eroded and enter the lakes than soils collected from the "likely to be eroded areas", such as surfaces of stream beds and sloping areas around the catchments. Due to the high contents of moss remains in the soils, which diluted Pb concentrations, the mean Pb concentration in the Loch Chon soil samples (40.5 mg kg^{-1}) was significantly lower than the estimated minerogenic concentration (51.1 ± 6.6 mg kg^{-1}) based on the pre-industrial Pb concentration in a sediment core from the lake [12]. The other site clearly affected by this issue is Loch Coire Fionnaraich where the mean Pb concentration in the catchment samples (31 mg kg^{-1}, Table 2) was significantly lower than its value in fresh sediments (36.6 mg kg^{-1}, Table 3). Since η_d is clearly greater than η_c, it follows from equation 2 that the value of η_c must lie between 0 and η. Further, an upper limit to the value of the direct fallout fraction F_d can be calculated by setting $\eta_c = 0$. For Lochs Coire Fionnaraich and Chon the values of these upper limits are 2.4% and 4.1% respectively. This appears to be less of a problem at the other three sites where values of F_d calculated using the measured values of η_c

(though discarding the obvious outlier in Round Loch of Glenhead) range from 1.3% in Round Loch of Glenhead to 3.9% in Burnmoor Tarn. Upper limits for these sites calculated by setting $\eta_c = 0$ range from 2.3% in Glenhead to 6.7% in Burnmoor. The results, set out in Table 4, show conclusively that catchment inputs are the dominant source of Pb to these UK lakes and that direct fallout accounts for no more than around 5% of total inputs.

Table 4. Estimates and upper limits of the fraction of total Pb in freshly deposited lake sediments attributable to direct atmospheric fallout,

Sites	Estimate	Upper limit	
	%	%	±1σ
Loch Coire Fionnaraich	-	2.4	0.35
Loch Chon	-	4.1	0.58
Round Loch of Glenhead	1.3	2.3	0.33
Burnmoor Tarn	3.9	6.7	0.34
Llyn Llagi	1.8	5	0.73

Inputs of minerogenic Pb occur regardless of any contribution from fallout onto the catchment, though they can be influenced by enhanced rates of soil erosion. Since minerogenic Pb locked up in mineral grains will be less available for take up by aquatic organisms, it is also of interest to consider the contribution of historical deposits of fallout Pb stored in catchment soils. Table 5 compares minerogenic Pb concentrations in Loch Chon, Round Loch of Glenhead, Burnmoor Tarn and Llyn Llagi to total Pb concentrations in fresh sediments, and also shows the fraction attributable to historical fallout. It follows that inputs of Pb to these lakes arising from atmospheric pollution stored in catchment soils over the past two hundred years are an order of magnitude higher than those due to contemporary fallout.

Table 5. Total Pb concentrations in freshly deposited sediments from 4 of the 5 lakes, minerogenic Pb concentrations, and the fraction attributable to inputs of fallout Pb stored in the catchment.

	Total Pb mg kg^{-1}	Minerogenic Pb mg kg^{-1}	Fallout fraction
Loch Chon	124	51	59%
Round Loch of Glenhead	236	49	79%
Burnmoor Tarn	187	40	79%
Llyn Llagi	166	75	55%

In the UK, atmospheric Pb emissions reached their highest level in 1973 at 9,300 tonnes, and since then have reduced hugely. In 2013, when the samples for this study were collected, UK Pb emissions were 63 tonnes.[7] Lead used to be an important pollutant entering UK lakes through atmospheric deposition but this is no longer the case. Previous studies[2-4] indicates that huge amounts of Pb have been deposited and stored in the lake catchments, and consequently, our data show that catchments could be a significant source of Pb to the lakes for many decades to come. We studied Pb budget in Lochnagar, a remote lake in Scotland, by a relatively big field investigation in monitoring atmospheric Pb deposition, investigating Pb distribution in the catchment soils and the lake sediments, and we roughly estimated that catchment inputs contributed 90% of total Pb into the lake, while atmospheric direct deposition contributed the other 10% in 1997.[6] UK Pb emissions in 1997 were 1,100 tonnes.[7] It suggests that with decline in Pb emissions to the environment, percentages of catchment Pb inputs in the total Pb entering the UK lakes have increased. Furthermore, when Pb deposition is the dominant source, the lake sediment record can be used for revealing historical trends in atmospheric pollution. However, now catchments have becomes the major Pb source, the lake sediments in the UK no longer reveal contemporary atmospheric Pb pollution[14] but rather, the scale of re-mobilisation of previously deposited Pb from catchment storage.

297 **3.5. Possibility of Using Mosses to Monitor Deposition.** In this study, two moss
298 species were used to represent atmospheric deposition for ^{210}Pb/Pb ratios. Here, we discuss the
299 possibility for doing so. Our previous study[16] suggests that, in low precipitation areas, if rainfall
300 is not sufficient for moss growth, then they may take water and nutrients from surrounding
301 soils. For example, terrestrial mosses took 77% of their Pb from soils in Richmond Park in
302 London,[16] where mean values of ^{210}Pb/Pb ratios in rain waters and mosses are 96 and 22 Bq
303 mg^{-1}, respectively, suggesting that mosses in Richmond Park might not be able to represent the
304 atmospheric deposition there. The values of ^{210}Pb/Pb ratios in the moss samples collected from
305 the lake sites in this study (240 – 810 Bq mg-1, Table 1) are more than double those in the
306 rainwaters collected in London, and are more than one order of magnitude higher than those in
307 the London mosses. Lead concentrations in the London mosses are high compared with those
308 at our lake sites, and this could reduce their ^{210}Pb/Pb ratios in the London mosses. However,
309 Pb concentrations in the Burnmoor Tarn mosses are similar to those in London, and hence,
310 high ^{210}Pb/Pb ratios are due to high ^{210}Pb deposition and high moss absorption. ^{210}Pb/Pb ratios
311 in our lake site moss samples are an order of magnitude higher than those in the surface soils
312 around them, and hence ^{210}Pb/Pb ratios in the moss samples are dominated by rainfall. In this
313 study, ^{210}Pb/Pb ratios in the mosses are used to represent depositions and resulting fractions of
314 Pb contributions from the catchment inputs to the lakes are higher than 95% (except Burnmoor
315 Tarn where the catchment contribution is more than 93%). However, if the mosses have been
316 affected by intake from soils to any degree, then this would lower the calculated fractions of
317 direct atmospheric Pb deposition. These are already very low and therefore any impact from
318 soil uptake would have little effect on our calculations and confirms that it is reasonable to use
319 ^{210}Pb/Pb ratios in mosses to represent those in the rainfall at these lake sites for this study. Moss
320 growth is directly related with and controlled by rain frequency and amount.[24,32] In areas with
321 high rain frequency and plenty of rainwater that provide sufficient nutrients and water for moss

growth, impact of ground nutrients on the mosses is negligible, resulting in that Pb isotope signature in the mosses is close to or dominated by atmospheric deposition. Mosses growing in relatively dry areas such as Richmond in London (annual rainfall c. 650 mm) may be affected severally by the ground soils, but it is reasonable to use mosses in the areas with frequent wet days and high rainfall (annual rainfall >2000 mm) to represent or monitor atmospheric deposition.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. Wu, J.F.; Boyle, E. A. Lead in the western North Atlantic Ocean: Completed response to leaded gasoline phase-out. *Geochim. Cosmochim, Acta*, **1997**, 61: 3279-3283.
2. Cloy, J. M.; Farmer, J. G.; Graham, M. C.; MacKenzie, A. B. Retention of As and Sb in ombrotrophic peat bogs: Records of As, Sb, and Pb deposition at four Scottish sites. *Environ. Sci. Technol*. **2009**, 43:1756-1762.
3. Farmer, J. G.; Graham, M. C.; Bacon, J. R.; Dunn, S. M.; Vinogradoff, S. I.; MacKenzie, A. B. Isotopic characterisation of the historical lead deposition record at Glensaugh, an organic-rich upland catchment in rural N.E. Scotland. *Sci. Total Environ*. **2005**, 346: 121-137.
4. Yang, H.; Rose, N.; Boyle, J.; Battarbee, R. Storage and distribution of trace metals and spheroidal carbonaceous particles (SCPs) from atmospheric deposition in the catchment peats of Lochnagar, Scotland. *Environ. Pollu*. **2001**, 115: 231-238.
5. Miller, H.; Croudace, I. W.; Bull, J. M.; Cotterill, C. J.; Dix, J. K.; Taylor, R. N. A 500 year sediment lake record of anthropogenic and natural inputs to Windermere (English

Lake District) using double-spike lead isotopes, radiochronology, and sediment microanalysis. *Environ. Sci. Technol*. **2014**, 48: 7254-7263.
6. Yang, H.; Rose, N.; Battarbee, R. W.; Boyle, J. F. Mercury and lead budgets for Lochnagar, a Scottish mountain lake and its catchment. *Environ. Sci. Technol*. **2002**, 36: 1383-1388.
7. NAEI, National Atmospheric Emissions Inventory. 2015. http://naei.beis.gov.uk/data/data-selector-results?q=104885 (accessed on 30/12/2017).
8. Torseth, K.; Aas, W.; Breivik,K.; Fjaeraa, A. M.; Fiebig, M.; Hjellbrekke, A. G. Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972-2009. *Atmospheric Chemistry and Physics*, **2012**, 12: 5447-5481.
9. Shotyk, W.; Weiss, D.; Appleby, P. G.; Cheburkin, A. K.; Frei, R.; Gloor, M.; Kramers, J. D.; Reese, S. History of atmospheric lead deposition since 12,370 14C yr BP from a peat bog, Jura Mountains, Switzerland. *Science* **1998**, 281: 1635-1640.
10. Shotyk, W.; Appleby, P. G.; Bicalho, B.; Davies, L.; Froese, D.; Grant-Weaver, I. Peat bogs in northern Alberta, Canada reveal decades of declining atmospheric Pb contamination. *Geophys. Res. Lett*, **2016**, 43: 9964-9974.
11. Rose, N.L.; Yang, H.; Turner, S. D.; Simpson, G. L. An assessment of the mechanisms for the transfer of lead and mercury from atmospherically contaminated organic soils to lake sediments with particular reference to Scotland, UK. *Geochim. Cosmochim. Acta* **2012**, 82: 113-135.
12. Yang, H.; Rose, N. Trace element pollution records in some UK lake sediments, their history, influence factors and regional differences. *Environ. Intern*. **2005**, 31: 63-75.
13. Farmer, J. G.; MacKenzie, A. B.; Graham, M. C.; Macgregor, K.; Kirika, A. Development of recent chronologies and evaluation of temporal variations in Pb fluxes and sources in lake sediment and peak cores in a remote, highly radiogenic environment, Cairngorm Mountains, Scottish Highlands. *Geochim. Cosmochim. Acta*. **2015**, 156: 24-49.
14. Yang, H. Lake sediments may not faithfully record decline of atmospheric pollutant deposition. Environ. *Sci. Technol*. **2015**, 49: 12607-12608.
15. Tebaldi, C.; Hayhoe, K.; Arblaster, J. M.; Meehl, G. A. Going to the extremes. *Climate Change*, **2006**, 79: 185-211.
16. Yang, H.; Appleby, P. G. Use of lead-210 as a novel tracers for lead (Pb) sources in plants. *Scientific Reports*, **2016**, 6, 21707; DOI 10.1038/srep21707.
17. Monteith, D.T, Evans, C.D., Eds. UK Acid Waters Monitoring Network: 10 Year Report. ENSIS Publishing, 2000.
18. Blomqvist, S.; Kofoed, C. Sediment trapping – A subaquatic in situ experiment. *Limnol. Oceanogr*. **1981**, 26: 585-590.
19. Renberg, I.; Hansson, H. HTH sediment corer. *J. Paleolimnol*., **2008**, 44: 655-659.
20. Appleby, P.G.; Richardson, N.; Nolan, P. J. Self-absorption corrections for well-type germanium detectors. *Nucl. Inst. & Methods B* **1992**, 71: 228-233.
21. Markert, B.; Herpin, U.; Siewers, U.; Berlekamp, J., Lieth, H. The German heavy metal survey by means of mosses. *Sci. Total Environ*. **1996**, 182: 159-168.

22. Reimann, C.; Niskavaara, H.; Kashulina, G.; Filzmoser, P.; Boyd, R.; Volden, T. Critical remarks on the use of terrestrial moss (Hylocomium splendens and Pleurozium schreberi) for monitoring of airborne pollution. *Environ. Pollut*. **2001**, 113, 41-57.
23. Yang, H.; Rose, N.; Battarbee, R. Distribution of some trace metals in Lochnagar, a Scottish mountain lake ecosystem and its catchment. *Sci. Total Environ*. **2002**, 285: 197-208.
24. Krebs, M.; Gaudig, G.; Joosten, H. Record growth of Sphagnum papillosum in Georgia (Transcaucasus): rain frequency, temperature and microhabitat as key drivers in natural bogs. *Mires and Peat*, **2016**, 18: Article 04, 1-16. DOI 10.19189/MaP.2015.OMB.190
25. Rothwell, J.J.; Evans, M.G.; Lindsay, J B. Scale-dependent spatial variability in peatland lead pollution in the southern Pennines, UK. *Environ. Pollut*. **2007**, 145: 111-120.
26. Wedepohl, K. H. The composition of the continental crust. *Geochim. Cosmochim, Acta*, **1995**, 59: 1217-1232.
27. Reimann C., Caritat, P. Chemical Element in the Environment – Factsheets for the Geochemist and Environmental Scientist. Springer-Verlag Berlin Heidelberg New York, 1998.
28. Sigg, L.; Sturm, M.; Kistler, D. Vertical transport of heavy-metals by settling particles in Lake Zurich. *Limnology Oceanography*, **1987**, 32: 112-130.
29. Taillefert, M; Gaillard, J. F. Reactive transport modeling of trace elements in the water column of a stratified lake: iron cycling and metal scavenging. J.Hydrology, **2002**, 256: 16-34.
30. Hargrave, B.T.; Burns, N.M. Assessment of sediment trap collection efficiency. *Limnology and Oceanography*, **1979**, 24: 1124-1136.
31. Bloesch, J.; Burns, N.M. A critical review of sedimentation trap technique. *Swiss Journal of Hydrology*, **1980**, 42, 15-55.
32. Bjerke, JW; Bokhorst, S.; Callaghan, T.V.; Phoenix, G. K. Persistent reduction of segment growth and photosynthesis in a widespread and important sub-Arctic moss species after cessation of three years of experimental winter warming. *Functional Ecology*, **2017**, 31: 127-134.